Macromolecules 2014 vol.47 N22, pages 7917-7929

Field-cycling NMR relaxometry probing the microscopic dynamics in polymer melts

Hofmann M., Kresse B., Privalov A., Willner L., Fatkullin N., Fujara F., Rössler E.
Kazan Federal University, 420008, Kremlevskaya 18, Kazan, Russia

Abstract

© 2014 American Chemical Society. Field-cycling (FC) 1H and 2H NMR relaxometry is applied to linear polybutadiene (PB) of different molar mass (M) in order to test current polymer theories. Applying earth field compensation, five decades in the frequency dependence of the spin-lattice relaxation rate T1 -1(v) = R1(v) are accessed (200 Hz - 30 MHz), and we focus on the crossover from Rouse to entanglement dynamics. A refined evaluation is presented, which avoids application of frequency-temperature superposition as well as Fourier transformation. Instead, the power-law exponent ∈ in the entanglement regime is directly determined from the susceptibility representation χNMR ′(ω) = ω/T1(ω) ω∈ by a derivative method. Correspondingly, a power-law t-∈ characterizes the decay in the time domain, i.e., the dipolar correlation function. For the total 1H relaxation, comprising intra- and intermolecular relaxation, a high-M exponent ∈total = 0.31 ± 0.03 is found. An isotope dilution experiment, which yields the intramolecular relaxation reflecting solely segmental reorientation, provides an exponent ∈intra = 0.44 ± 0.03. It agrees with that of FC 2H NMR (∈Q = 0.42 ± 0.03) probing only segmental reorientation. The fact that ∈intra > ∈total demonstrates the relevance of intermolecular relaxation in the entanglement regime (but not in the Rouse regime), and ∈intra is significantly higher than predicted by the tube-reptation (TR) model (∈TR = 0.25) and, the latter being supported also by recent simulations. The ratio of inter- to intramolecular relaxation grows with decreasing frequency, again in contradiction to the TR model and results from double quantum 1H NMR. We conclude that no clear evidence of a tube is found on the microscopic level and the so-called return-to-origin hypothesis is not confirmed. Studying the influence of chain end dynamics by FC 1H NMR we compare differently chain end deuterated PB. For the dynamics of the central part of the polymer the exponent drops from ∈intra = 0.66 ± 0.03 down to ∈cent = 0.41 ± 0.03 for M = 29k which is very close to the high-M value ∈intra. Thus, the protracted transition to entanglement dynamics reported before is not found when the polymer center is probed; instead full entanglement dynamics appears to set in directly with M > Me.

http://dx.doi.org/10.1021/ma501520u